

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : C09K 5/00		A1	(11) International Publication Number: WO 96/37570
			(43) International Publication Date: 28 November 1996 (28.11.96)
(21) International Application Number: PCT/US96/07659 (22) International Filing Date: 24 May 1996 (24.05.96) (30) Priority Data: 08/449,338 24 May 1995 (24.05.95) US (71) Applicant: EVANS COOLING SYSTEMS, INC. [US/US]; 253 Route 41 North, Sharon, CT 06069 (US). (72) Inventor: EVANS, John, W.; 255 Route 41 North, Sharon, CT 06069 (US). (74) Agents: SAMPLES, Kenneth, H. et al.; Fitch, Even, Tabin & Flannery, Room 900, 135 S. LaSalle Street, Chicago, IL 60603 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.	
(54) Title: NON-AQUEOUS HEAT TRANSFER FLUID AND USE THEREOF			
(57) Abstract			
A composition and method of cooling a heat exchange system comprising: a composition consisting essentially of propylene glycol; and at least one of a molybdate salt, a nitrate compound and an azole compound.			
BEST AVAILABLE COPY			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CJ	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**BEST AVAILABLE COPY**

- 1 -

**NON-AQUEOUS HEAT TRANSFER FLUID AND USE THEREOF****CROSS-REFERENCE TO RELATED APPLICATION**

5 The present application is a continuation-in-part of patent application U.S. Serial No. 08/409,026, filed March 23, 1995, which is a continuation-in-part of patent application U.S. Serial No. 08/119,514, filed September 10, 1993.

10 **BACKGROUND OF THE INVENTION**

The present invention relates generally to a substantially non-aqueous heat transfer fluid for use in a heat exchange system and, particularly, to a coolant for internal combustion engines.

15 The coolants that are currently used create continuing environmental problems and raise concerns about toxicity, health effects and disposal problems. In particular, toxicity leading to acute short term oral health effects of coolants upon humans and other mammals is problematic. In addition, chronic health problems associated with coolants often relate to contamination from elemental heavy metal precipitates and toxic inhibitors that are added for water related reactions.

20 Every year nearly 700 million gallons of antifreeze are sold in the U.S. alone, and about 1.2 billion gallons are sold worldwide. The problem of the inherent toxicity of currently used coolants is exacerbated by estimates that 25% to 50% of this volume is disposed of improperly. One major cause of this pollution is dumping by consumers. While increased consumer awareness can be achieved through education, improper disposal will remain a problem.

30 Another major source of improper disposal emanates from leakage, spills and overflows in the heavy duty

- 2 -

truck and off-road vehicle industry. Experience with heavy duty vehicles shows that it is common to lose 10% of the coolant volume every 12,000 miles (19,312 km) to 18,000 miles (28,967 km). This equates to a leakage rate of one drop per minute, or one gallon per month for the typical highway truck. Even though a coolant leak this small is likely to go unnoticed, it can accumulate into a significant loss. For example, many heavy duty fleets never change coolant but purchase enough antifreeze for loss replacement every year to replace all of the coolant in each of their vehicles.

In some heavy-duty operations, overflows and venting losses account for far more coolant loss than the previously mentioned leaks at the water pump, hose clamps or radiator core. When a heavy-duty truck radiator without an overflow tank is topped off, a quart or more of coolant is usually lost due to overflow from the coolant expanding upon heating of the engine. It is to be noted that even if small spills and leaks of coolant eventually biodegrade with little impact upon the environment, such leaks present a toxic danger to wildlife while they exist as a liquid and by contamination of heavy metals they carry (suspended), due to cooling system erosion and corrosion.

Current formulations of engine coolants typically utilize the characteristics of water as the primary heat removal fluid. The water content of a coolant is typically 30% to 70% by weight, depending upon the severity of the winter climate.

Another component of a conventional engine coolant is a freeze point depressant. Currently, the freeze point depressant in most cases is ethylene glycol (EG), which is used in a range of 30% to 70% by volume to prevent freezing of the water during winter. In some warm

SUBSTITUTE SHEET (RULE 26)

BEST AVAILABLE COPY

- 3 -

weather areas, freezing temperatures are not encountered and water with only a corrosion inhibitor package is used.

Moreover, an additive package containing numerous  
5 different chemicals is initially added to the freeze point depressant to form an antifreeze concentrate, and eventually blended with water to form the coolant. These additives are designed to prevent corrosion, cavitation, deposit formation and foaming, and are each  
10 in concentrations of 0.05% to 3% by weight of the final coolant.

Recently propylene glycol (PG), with inhibitors, has gained some acceptance as a freeze point depressant, mostly because of its lower toxicity rating than EG.  
15 It is the water fraction and the delicate balance of the water content to the freeze point depressant that has thwarted attempts by vehicle manufacturers and coolant formulators to develop a "world coolant" which is applicable from the arctic to the tropics and to all  
20 engines; light and heavy duty. Currently a ratio of 70% EG concentrate to 30% water is required for the arctic, but this ratio is not acceptable (due to convective transfer loss) in the tropics which typically require a 40% EG to 60% water ratio. Additionally the heavy duty  
25 engine manufacturers require a high concentration of sodium nitrate, as an additive for iron cavitation (see below), which is not desirable in light duty engines. The complexity of balancing various water to EG (or PG) ratios and different additive formulations has created a  
30 recurring problem in the field of improper freeze protection and clogged radiators and heater cores, due to mis-formulation of inhibitor additives. These problems, as will be discussed further below, exist because of the need for a substantial water fraction in

- 4 -

the make-up of the cooling fluid, termed an "aqueous coolant".

5 In addition, contaminants build up in the coolant as the engine is used and result from thermal and oxidative breakdown of glycol, lube oil and fuel accumulation, or metal corrosion and erosion products from the cooling system components.

10 Finally, as mentioned above, supplemental coolant additives are used in heavy duty service to prevent cavitation erosion of cylinder liners (iron) and to replenish inhibitor chemicals depleted with service. Supplemental coolant additives are not used or required in passenger cars which have a coolant life of 20,000 miles (32,186 km) to 30,000 miles (48,279 km). Heavy-duty service usually demands 200,000 miles (321,860 km) to 300,000 miles (482,790 km) before coolant replacement and hence the need to periodically replenish inhibitors. Examples of commonly used supplemental coolant additives include sodium nitrate, dipotassium phosphate, sodium molybdate dihydrate, and phosphoric acid.

20 Cylinder liner cavitation is another prime example of the complex reactions which occur when a substantial portion of the coolant is made up of water. When, for example, a mixture of 50% water and 50% EG is used (50/50 EGW) in a heavy duty engine the vapor pressure of the coolant is very high, about 600 mm/Hg, and under high load conditions large amounts of water vapor are produced on the coolant side of the cylinder wall. As the water vapor ultimately collapses around the cylinder wall, the energy released from the phase change (gas to liquid) impacts the wall and small amounts of iron are eroded, on an ongoing basis. Sodium nitrate is added to chemically limit the amount of vapor impacting the cylinder wall.

- 5 -

Supplemental coolant additives must be chemically balanced with the coolant volume, which is costly to control and can be catastrophic to the cooling system components, and the engine, if improperly done. If the amount of the supplemental coolant additives in the coolant is too low, corrosion and cavitation damage to the engine and cooling system components will occur, but if the amount is too high, additives will "fall-out" of solution and eventually clog radiator and heater cores. Another difficulty with supplemental coolant additives is that they are difficult to properly dissolve in an aqueous solution and may resist going into a final solution, as a supplemental additive, which causes additional clogging problems.

The acute oral toxicity of spent antifreeze is largely determined by the amount of ethylene glycol used. Thus, additives and contaminants have a lesser effect on coolant toxicity. Regardless of size, spills and leaks can pose an acute oral toxicity danger to wildlife and pets.

Glycols make up 95% by weight of the antifreeze/coolant concentrate, and after blending with the water, about 30% to 70% by volume of the coolant used in the vehicle. Conventional antifreeze has for years been formulated with EG.

A major disadvantage of using EG as a freeze point depressant for engine coolants is its high toxicity to humans and other mammals if ingested. Toxicity is generally measured in accordance with a rating system known as the LD<sub>50</sub> rating system, which is the amount of substance expressed in grams per kilogram of body weight, when fed to laboratory rats in a single dose, which will cause an acute oral toxic poisoning. A lower LD<sub>50</sub> value indicates a higher toxicity (smaller amounts

- 6 -

of substance required to be lethal). An LD<sub>50</sub> rating of less than or equal to 20.0 grams of substance per kilogram of body weight can classify a material as hazardous. Thus, because EG has an LD<sub>50</sub> rating of 6.1 g/kg, EG is hazardous by this rating system. Moreover, EG is a known toxin to humans at relatively low levels, reported as low as 0.398 g/kg. Consequently, EG is classified by many regulatory authorities as a dangerous material. When ingested, EG is metabolized to glycolic and oxalic acids, causing an acid-base disturbance which may result in kidney damage. EG also has the added complication of a sweet smell and taste thereby creating an attraction for animals and children.

In addition to the difficulties that arise from the use of EG, serious problems may result from the instability of the additives that are used in current coolant formulations. An EG-based concentrate requires 3% to 5% water content in order not to freeze at +7.7°F (-13.5°C). Water is also added to all known coolant concentrates so that additives can be dissolved during formulation and remain in suspension during extended periods of storage.

Although a small amount of water, as discussed above, is intentionally added to EG/PG concentrate to keep the water soluble additives in solution, while being stored, it is not adequate for long periods of time. The additives must be agitated, periodically, in order to remain in solution until added to water as a final coolant mixture. If storage as a concentrate is too long a period (over 6-8 months) then the water soluble additives begin to "fall-out" of suspension and will accumulate in the bottom of the container as a "gel". The "gelled" additives will not return to solution even with agitation. This problem, however, is

- 7 -

not limited to the stored concentrate only. Even when fully mixed, as 50/50 EG or PG, the water soluble additives will "gel-out" if not agitated (the engine run) regularly. This can be a severe problem for engines used in stationary emergency pumps and generators as well as military and other limited use engines.

One difficulty with the large water fraction of the diluted engine coolant, typically a 50/50 ratio of concentrate to water, is the emergence of precipitates of heavy metals, such as lead and copper contaminants, that become suspended in the water portion of the circulating coolant in the engine. The water reacts with lead and copper materials from radiators which are the source of not only brass, and thereby copper, but also lead solder.

Water is also highly reactive with light alloys, such as aluminum, and the water fraction of the coolant can generate large amounts of aluminum precipitates, which increases at an increasing proportion with higher coolant temperatures. Water soluble additives are used for these reactions, but cannot totally eliminate the reaction, and aluminum is constantly lost to the 50/50 EG or PG coolant.

Cooling systems contain many different metals and alloys, and corrosion of these metals by coolants has been unavoidable because of the inclusion of water with the diol-based antifreezes, such as ethylene glycol or propylene glycol. Corrosion occurs because of the formation of organic acids in the coolant, such as pyruvic acid, lactic acid, formic acid, and acetic acid. The organic diols produce acidic oxidation products when in the presence of hot metal surfaces, oxygen from either entrapped air or water, vigorous aeration, and

- 8 -

metal ions, each of which catalyze the oxidation process. Moreover, formation of lactic acid and acetic acid is accelerated in coolant solutions at 200°F (93.3°C) or above while in the presence of copper.

5      Formation of acetic acid is further accelerated in the presence of aluminum in coolant solutions at 200°F (93.3°C) or above.

Among the metals and alloys found in cooling systems, iron and steel are the most reactive in the formation of acids, whereas light metals and alloys, such as

10      aluminum, are considerably less reactive. As the oxidation of diols progresses, the level of organic acids formed with the water fraction rises and the pH of the coolant decreases, and therefore the corrosion of

15      the metal surfaces increases.

Currently known and utilized coolants include buffers to counteract these organic acids. The buffers act to create a coolant with a higher initial pH of approximately 10 or 11. Thus, as the oxidation occurs,

20      the pH decreases accordingly. Some examples of typically utilized buffers include sodium tetraborate, sodium tetraborate decahydrate, sodium benzoate, phosphoric acid and sodium mercaptobenzothiazole.

Buffers, in turn, also require water in order to enter into and remain in solution. As the buffer

25      portion of the solution becomes depleted over time, the water fraction of the coolant reacts with the heat, air and metals of the engine, and as a result, the pH decreases because of the acids that form. Thus,

30      corrosion remains a large problem in coolants that utilize water.

In fact, all known coolant formulations require the addition of water to solubilize additives used as buffers and anti-foam agents and for prevention of

SUBSTITUTE SHEET (RULE 26)

- 9 -

aluminum corrosion. Examples of such additives include phosphates, borates, silicates or phosphoric acids. In addition, these water soluble additives require heat, extreme agitation, and extensive time for the water to react and cause the additives to dissolve.

These requirements add significant cost and complexity to the formulation and packaging of antifreeze concentrates. The energy costs and time required for blending, before packaging, are a major factor in the processing costs. Also, the constant requirement to monitor the formulating process to assure a "proper blend" has become extremely costly as many of today's additives, for aqueous concentrates, interfere with each other and can cause an incomplete solution and failure of the formulation process.

All currently used and previously known coolants require inhibitors to control the corrosive effects from the required water content. The inhibitors must be balanced so that they do not react with each other because that would otherwise minimize their individual purposes. For instance, phosphates and borates would decrease the protection of silicates on aluminum. Moreover, the inhibitors must not be in excess concentration, which is usually done to extend the depletion time, because that causes damage to system components. For example, "fall-out" from solution causes plugging of radiators and heaters. In addition, silicates, silicones, borates and phosphates are abrasive and erode heat exchanger tubes and pump impellers. Nevertheless, the inhibitors must still exist in a concentration which is adequate to protect all metals.

Thus, the additive package that is included in known coolant formulations typically consists of from 5 to 15

- 10 -

different chemicals. These additives are broken down into major and minor categories, depending upon the amount used in an engine coolant formulation:

<u>MAJOR (0.05% to 3%)</u>	<u>MINOR (&lt;0.05%)</u>
Buffer	Defoamer
Corrosion inhibitors	Dye
Cavitation inhibitors	Scale inhibitor
	Surfactant
	Chelates

In addition, some of the additives themselves are considered toxic, such as borates, phosphates, and nitrates. Thus, not only do all known coolant formulations include additives that require heat, extreme agitation and extensive time for the water to react and cause the additives to dissolve, but the additives themselves are sometimes toxic. Further, the additives require complex balancing which accommodates the prevention of interference between the additives, while also preventing the excessive presence of any one additive in the coolant.

#### SUMMARY OF THE INVENTION

The present invention solves the aforesaid problems by providing a propylene glycol (PG) based coolant that is essentially non-aqueous. The coolant does not have a substantial amount of water. The utilization of a "neat" (substantially water-free), PG base liquid, as well as "neat" PG dissolvable corrosion inhibitors, allows the formulation of the present invention to require much less time to blend, to be lower in blending costs and to be less problematic. The instant invention, of a substantially water-free diol coolant (preferably propylene glycol) utilizes a unique

- 11 -

formulating process (with all the previously mentioned benefits), which will be further detailed below along with the unique characteristics of the fully formulated coolant as being the first single formula "world  
5 coolant". The invention creates a coolant with a stable solution of inhibitors which has a long term shelf life, is non-hazardous with low toxicity and will not freeze in a "neat" state, in either storage or in use.

A cooling system such as disclosed in U.S. Patent  
10 Nos. 4,550,694 and 5,031,579 which utilizes the PG based coolant in accordance with the present invention can advantageously operate at a significantly lower pressure at or near ambient level, while also restricting water absorption. Not only does the system thereby allow for  
15 a simple and stable additive package, but the reduced pressure of the cooling system also eliminates stress of the components. The innate lubricous nature of the coolant of the present invention is benign to rubber, and allows the pump seals, hoses and system components  
20 to normally last 150,000 miles (241,395 km) or more, which dramatically lowers the loss of coolant to the environment because of leaks, while also decreasing overheating.

The fully formulated non-aqueous coolant will operate  
25 in any engine constructed similarly to those disclosed in the aforementioned patents, and under any environmental conditions from -70°F ambients to +130°F or more. It is applicable in the artic or the tropics, with no changes required. Because it is non-aqueous  
30 there are no mixture ratios to change, for different environments, and the additives, (all PG soluble), will stay in suspension, without agitation, for many years of storage. There is no need for a heavy duty engine formulation because there is no cylinder liner

- 12 -

cavitation with non-aqueous PG, (which will be further described below), and therefore no need for the addition of sodium nitrate. The instant inventions unique coolant formulation of one fluid, with one stable  
5 additive package, that is long life and operable in all environments without mixture changes, or re-inhibiting of additives, makes the formulation the first truly "world coolant".

The lack of water in the formulated PG based coolant  
10 of the present invention also substantially reduces, and in most instances eliminates, the problem of contamination from precipitates of heavy metals, such as lead and copper. Thus, the non-aqueous nature of the present invention also decreases the toxicity level of  
15 the coolant. Also, because uniquely, pH (acidity) is not a factor with the non-aqueous formulated coolant of the present invention, which will be further discussed later, there is no need for toxic additives such as borates and phosphates. Also since there are no  
20 cavitation erosion problems the toxic additive sodium nitrate is also no longer necessary. Therefore it can clearly be seen that the unique water-free, diol formulation results in an extremely low toxicity rating and produces a non-hazardous, environmentally friendly  
25 coolant.

The aforesaid freedom from cavitation erosion of cylinder liners, in heavy duty engines, is also a unique feature attributable to the water-free diol formulation of the present invention. With an extremely low water  
30 content it was found that the vapor pressure of the fluid remains very low (about 30 mm/Hg) and the vapor, which is normally produced along the cylinder wall, is totally eliminated. The elimination of the cylinder wall vapor completely stops the occurrence of wall

- 13 -

erosion from cavitation. Because there is no cavitation erosion there is no need for the addition of sodium nitrite (which is water soluble only), which negates the need to add water for the dissolving of the additive, if  
5 it were required. It is surprising to find the complex benefits of a substantially water-free coolant and how one corrected problem originally caused by the existence of water (cavitation) eliminates the need to add water (dissolving of sodium nitrate with water).

10 Because the coolant of the present invention is initially free of water, and the system with which the coolant is used isolates the hot coolant from air and moisture, there is no major chemical reaction from which significant levels of acids may be formed. Since two of  
15 the major catalysts for acid formation, air and water, are nonexistent at the outset, as well as through the life of the system, there is no reason to add buffering agents in the formulation of the coolant. Therefore, the need to raise the water content of the coolant for  
20 additive solubility is eliminated, because only PG soluble additives need to be employed. Further, the coolant formulation of the present invention can accommodate the existence of water, preferably below a concentration of 0.25% by weight, as an impurity, and  
25 during use water (absorbed as a contaminant) can be permitted in concentrations of preferably below about 5.0% by weight, without requiring any buffering agents.

The water-free nature of the coolant formulation and systems operation of the present invention also  
30 eliminates other water, air, heat and metal based reactions and their water soluble additives. The reactions and additives that are eliminated include:

1. Anti-foam reactions/Silicones and polyglycol additives,

SUBSTITUTE SHEET (RULE 26)

- 14 -

2. Aluminum corrosion/Silicates,
3. Cavitation corrosion/Nitrites,
4. Scale inhibitors/Polyacrylates, and
5. Anti-fouling/Detergents.

5       Whereas the water soluble additives of known coolants  
require heat, extreme agitation and extensive time for  
the water to react and cause the additives to dissolve,  
the present invention utilizes a preferred additive  
package of three PG liquid soluble additives which do  
10       not require water to enter into or remain in solution,  
require no heat and only a short time to dissolve, with  
only slight agitation needed.

      The formulation may be prepared by two different  
methods. Method (1) includes the formation of a liquid  
15       solution of additives and a diol fluid (preferably  
propylene glycol) which are pre-mixed in a concentration  
"additive" tank and, after complete solution is  
achieved, are then finally blended into the bulk tank  
which is filled with industrial grade PG diol coolant  
20       (rated less than .01% water content, by weight). Method  
(2) includes the introduction of the additives in powder  
form directly into the bulk blending tank which is  
filled with bulk PG diol coolant (same industrial  
grade).

25       Recycling of the coolant of the present invention is  
easier and less costly than in known coolant  
formulations. During recycling, distillation of aqueous  
coolants is costly and time consuming. Because water is  
restricted to minimal amounts in the present invention,  
30       the requirement of distilling out the water fraction is  
substantially reduced or eliminated. Thus, recycling of  
the present invention simply involves filtering out  
suspended solids and old additives, with distillation  
requirements greatly reduced or eliminated.

- 15 -

The present invention is also more conducive to storage. Aqueous coolants and additives suffer from "fall-out" of additives during extended storage, but the additives of the present invention, which do not require water to remain in solution, can be maintained in long periods of storage without the need for periodic agitation.

Because it is intended that this coolant will become a "world coolant" the unique feature of extended storage capability is extremely important. As the supply line fills with a "mono-coolant," multiple mixtures will become single items and the shelf aging will significantly increase to much longer intervals. These extended periods will not be of concern, however, because the coolant formulation will remain stable, no matter how long the storage period, and dissolved additives will not "fall-out" of solution causing improper corrosion protection and transient additive gels which can clog radiators and heater cores. It should be noted that should the non-aqueous coolant be required to merely add one water soluble inhibitor, into the formulation, then the above described extended shelf life would not exist and a major feature of the present invention will be lost. This, of course, is not the case as it is interrelated to the unique substantially water-free, low acidity discovery of the invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

In a preferred embodiment of the invention, PG is chosen as the essentially non-aqueous heat transfer base liquid. PG has an LD<sub>50</sub> rating of 33.7 g/kg and is therefore non-hazardous. Moreover, PG has an acrid taste and smell and is thus not attractive to animals. "Neat" PG provides a lower freezing point than EG and

- 16 -

does not require the presence of water to function as a freeze point depressant. "Neat" PG freezes at  $-76^{\circ}\text{F}$  ( $-60^{\circ}\text{C}$ ), whereas "Neat" EG freezes at  $7.7^{\circ}$  ( $-13.5^{\circ}\text{C}$ ).

5 Although the preferred embodiment of the invention solely utilizes PG as the non-aqueous heat transfer base liquid, PG could be used in combination with EG. The use of EG in a mixture with PG, however, is not as beneficial as using PG alone because of increased toxicity. However, in order to retain the present  
10 invention's other characteristics, the mixture must contain at least 40% PG. A coolant utilizing such a mixture would retain some of the characteristics of the preferred embodiment, but would be more toxic and hazardous. Other glycols are much more toxic than PG.  
15 Diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, and ethylene glycol have LD<sup>50</sup> ratings of 16.6 g/kg, 14.8 g/kg, 22.0 g/kg, 3.0 g/kg, and 6.1 g/kg, respectively.

In addition, because of the high temperatures that  
20 can exist in an engine, the boiling point of the base liquid is also an important factor in formulating a coolant. Propylene glycol has a satisfactory boiling point of  $369^{\circ}\text{F}$  ( $187.2^{\circ}\text{C}$ ), but the boiling point of ethylene glycol,  $387.1^{\circ}\text{F}$  ( $197.3^{\circ}\text{C}$ ), is at the upper  
25 limit for acceptable boiling points. If the boiling point is higher, then the coolant and critical engine metal temperatures can become too hot. Other glycols have much higher boiling points, which are too excessive. For instance, diethylene glycol has a  
30 boiling point of  $472.6^{\circ}\text{F}$  ( $244.8^{\circ}\text{C}$ ), dipropylene glycol has a boiling point of  $447.8^{\circ}\text{F}$  ( $231^{\circ}\text{C}$ ), triethylene glycol has a boiling point of  $545.9^{\circ}\text{F}$  ( $285.5^{\circ}\text{C}$ ), and tripropylene glycol has a boiling point of  $514.4^{\circ}\text{F}$  ( $268^{\circ}\text{C}$ ).

- 17 -

5       The instant invention also utilizes only additives  
that are soluble in PG, and thus does not require water  
for the additives to enter into or remain in solution.  
In addition to being soluble in the PG, each chosen  
10       additive is a corrosion inhibitor for one or more  
specific metals. A nitrate compound, such as sodium  
nitrate, is utilized as an additive to inhibit corrosion  
for iron or alloys containing iron, such as cast iron.  
Although sodium nitrate's primary function is to prevent  
15       corrosion for cast iron, it also slightly inhibits  
solder and aluminum corrosion. An azole compound, such  
as tolyltriazole, functions as a corrosion inhibiting  
additive for both copper and brass. Moreover,  
tolyltriazole is also beneficial by slightly increasing  
20       the pH because of its basic effect. A molybdate  
compound, such as sodium molybdate, primarily functions  
as a corrosion inhibitor for lead from solder, but is  
also beneficial in decreasing corrosion for all other  
metals.

20       The choice of PG soluble additives thus depends on  
which metals are of concern with regards to corrosion.  
Currently, sodium nitrate, tolyltriazole and sodium  
molybdate would all be required to formulate a "world  
25       wide" coolant because of the presence of the particular  
metals currently in use in cooling system components.  
However, an additive could be reduced or eliminated if  
the particular metal it acts on is eliminated. For  
example, if lead-based solder is eliminated, then the  
content of sodium molybdate could be reduced, or would  
30       not be required at all.

The additives can be present in a range from a  
concentration of about 0.05% by weight to about 5.0% by  
weight, and more preferably not above about 3.0% by  
weight. Solutions below about 0.1% by weight are not as

- 18 -

effective for long life inhibition, while solutions over about 5.0% will suffer "fall-out." In the preferred embodiment, each additive is present in a concentration of about 0.3% to about 0.5% by weight depending upon the service life of the coolant.

Another attribute of the present invention is that neither magnesium nor aluminum corrosion occur, and additives for these purposes are therefore eliminated. Light alloys will not corrode with PG.

The preferred three additives exhibit many advantages. For instance, the additives are not rapidly depleted and may be formulated to last for heretofore unobtainable service periods, without change or additive replenishment for up to about 10,000 hours or 400,000 miles (643,720 km) in many forms of engines and vehicles. Another advantage of these PG liquid soluble additives which do not require water is that the additives go into suspension readily and remain in suspension, even in extreme concentrations, without falling out of solution, when each additive is present in concentrations of up to 5.0% by weight. Moreover, a significant degrading effect does not exist when the additives interact with each other. In addition, the additives are not abrasive, and the additives and coolant protect all metals, including magnesium, for a minimum of 4,000 hours or 150,000 miles (241,395 km).

The non-aqueous soluble additives in the present invention do not become depleted over extended hourly usage or mileage, and thus the need for supplemental coolant additives is ordinarily eliminated. Nevertheless, if it is desirable to add supplemental coolant additives, the non-aqueous formulation exhibits advantages because the supplemental coolant additives will more readily enter stable solution with the present

- 19 -

invention than in aqueous coolants. Moreover, the proper balance of supplemental coolant additives is easier to maintain, with a broad possible range of concentrations from about 0.05% by weight to about 5.0% by weight.

5 Here again the aforesaid advantages of the unique formulating process, of the present invention, also exist in the field if and when the supplemental addition of additives is required. The supplements may be added  
10 in either dry powder form, or as a dissolved concentrate directly to the cooling system. They may be added to a cool engine (50°F or above) and will dissolve into solution merely by idling the engine, without any chance of clogging the radiator, or heater cores. Also,  
15 because the target base solution is about 0.3% by weight and the saturated limit is about 5.0% there is no real chance of the mechanic adding an unacceptable amount of supplemental additive. Conversely, current water-based additives must be added to a hot coolant, then run hard  
20 (to enter solution) and are easily over saturated causing a common occurrence of radiator and heater damage.

For purposes of this invention, "non-aqueous" means water is present as an impurity in the coolant  
25 formulation, in no greater than a concentration of about 0.5% by weight. Although an increase in water is not desired during use, the present invention can accommodate the presence of some water. Because PG is a hygroscopic substance, water can enter the coolant from  
30 the atmosphere, or water can escape from the combustion chamber into the coolant from a combustion gasket leak into the cooling chamber. Although the essence of the invention is to avoid water, the invention will permit some water; however, increase of the water fraction

- 20 -

during use is preferably restricted to below about 5.0% by weight, and more preferably, below about 3.0% by weight. Further, the invention and related cooling systems can tolerate water up to a maximum concentration of about 10% by weight.

The coolant of the present invention remains non-hazardous in use with low toxicity in preferred compositions containing more than about 84.5% PG. The corrosion inhibitors used are also listed as non-hazardous by the EPA. In addition, these additives are used, preferably, in a concentration at or below about 0.3% by weight, which is considered non-hazardous by the EPA. Furthermore, the water content is preferably below about 0.25%, as formulated, and remains below about 5.0% in use which eliminates the precipitates of heavy metals and causes the coolant to remain non-hazardous in use and thus may be disposed of as such.

Aqueous coolants and cooling systems can cause the formation of entrapped air and violent vapor bubbles (cavitation) in the cooling system, and thus lead to high lead and copper erosion from the effects of the vapor/gases and the reaction of water with the metals. However, the present invention's non-aqueous nature eliminates the air and vapor bubbles and thus reduces the heavy metal precipitates. Moreover, tolyltriazole and sodium molybdate are utilized as corrosion inhibitors for these metals.

The elimination of water in the present invention relieves the coolant of catalysts that lead to acidic oxidation products. Not only is water itself involved in oxidation reactions in currently formulated coolants, but it is also a source for oxygen. Thus, if water is not present, or is at a minimal amount, corrosive effects on metals and alloys is dramatically reduced.

- 21 -

The pH scale reflects the acidity or alkalinity of an aqueous solution. Therefore, the pH scale is merely an indicator of acidity that will exist once air and water are present to form acids and react with the metal.

5 Because the present invention and the systems in which it is used avoid water, a coolant that would otherwise have a pH level as low as 3 or 4 if water were present would still not exhibit unacceptable corrosive effects on the metals and alloys in the engine.

10 As long as traditional acidity values remained a concern then the related formulation would always require buffering agents to make the initial coolant more "basic" (a higher pH of 10 to 14). With the addition of buffers; phosphates, borates, carbonates and  
15 the like, about 5% water must be added to the coolant formulation in order to cause these water soluble buffers to enter into solution. However, ultimately to remain in solution a water content of about 10% is needed in order to assure there is no "fall-out" of the  
20 buffering agents which would result in gelling and clogging of the cooling system. Hence more water content and more need for acidity control.

The preferred embodiment of the coolant formulation is as follows:

<u>Components</u>	<u>"A"</u> (Subject Coolant)	<u>"B"</u> (Conventional Coolant with Antifreeze Added)
1) Glycol		
30 a. Propylene wt. %	>99	-
b. Ethylene wt. %	-	46.75
2) Water wt. %	< 0.1	50.83
3) Tolyltriazole wt. %	0.3	0.10
4) Sodium Nitrate wt. %	0.3	0.05
35 5) Sodium Molybdate wt. %	0.3	0.05
6) Sodium Metaborate wt. %	-	0.50

SUBSTITUTE SHEET (RULE 26)

- 22 -

7)	Sodium Hydroxide wt. %	-	0.12
8)	Sodium Benzoate wt. %	-	1.50
9)	Sodium Nitrite wt. %	-	0.05
10)	Sodium Metasilicate wt. %	-	0.10

5

The compositions of the present invention may be prepared by the following methods:

(1) A. Concentrate Additive Tank; 400 Gals PG

\* Inhibitors;

10

- TTZ 5.0% by weight 168.0 lbs.
- Molybdate salts 5.0% by weight 168.0 lbs.
- Sodium Nitrate 5.0% by weight 168.0 lbs.

\* Blending time 20 mins./room temp 60°-70°F

\* Standard paddle or propeller, or air agitation

15

B. Bulk Final Formulation; (6500 gals total)

\* Main tank 6100 gals P.G./Industrial grade

\* Add concentration additive (400 gals)

\* Blending time 30 mins./room temp 60°-70°F

20

\* Standard paddle/prop, or air agitation

(2) Powder Direct Addition; (6500 gals. total)

\* Main tank bulk PG coolant 6500 gals.

\* Inhibitors; direct addition

25

- TTZ 0.3% by weight 168.0 lbs.
- Molybdate salt 0.3% by weight 168.0 lbs.
- Sodium Nitrate 0.3% by weight 168.0 lbs.

\* Blending time 1.5 hours/room temp 60°-70°F

\* Standard paddle/prop, or air agitation

30

Either method (1) or (2) will result in the same final solution of a stable fully formulated non-aqueous coolant in a period of time that is about 1/6 the time typically required (currently about 8 hours) to properly formulate the presently used Ethylene, or Propylene,

SUBSTITUTE SHEET (RULE 26)

- 23 -

Glycol antifreeze coolant concentrate.

Example 1 - Corrosion Test/Laboratory

[ASTM #D-1384 (Modified)]

5       The first example examines a corrosion test for  
engine coolants in glassware. Description: Six  
specimens, typical of metals present in an engine  
coolant system, are totally immersed in the test  
10       coolant. Normally the coolant is aerated, by bubbling  
air up through the glassware, and kept at a test  
temperature of 190°F (88°C) for 336 hours. These tests,  
however, and the results tabulated below, were performed  
with the following modifications to more effectively  
15       prove the benefits of the invention. Thus, both test  
coolants ("A" and "B") were operated at a control  
temperature of 215°F (101.6°C) to simulate severe duty  
use, and the subject coolant "A" was tested without  
aeration being applied in order to more closely  
approximate its operation in a non-aqueous cooling  
20       system as described in U.S. Patents 4,550,694; 4,630,572  
and 5,031,579. However, the conventional antifreeze,  
coolant "B," was aerated in the normal manner of the #D-  
1384 test. At the completion of the test, corrosion was  
measured by weight loss of each metal specimen.

25

Results

[ASTM #D-1384 (Modified)]

1)       Light Alloy Engines

(Aluminum or Magnesium Head and Block)

30	METAL	Δ WT	
		"A" COOLANT (Mg)	"B" COOLANT (Mg) ASTM STD.
	Magnesium	-1.3	>-1,000-
	Aluminum	+0.3	-21.1-30
35	Steel	-0.5	-3.9-10

- 24 -

Copper	-3.7	-7.4-10
Solder	-9.0	-19.2-30
Brass	-0.6	-5.1-10

- 5           2)           Combined Alloy Engines  
               (Aluminum [partial] with iron, or all iron)

METAL	$\Delta$ WT		ASTM STD.
	"A" COOLANT (Mq)	"B" COOLANT (Mq)	
Cast Iron	+1.0	-6.2	-10
10 Aluminum	+2.0	-18.6	-30
Steel	0	- 4.3	-10
Copper	-3.0	- 8.9	-10
Solder	-6.1	-19.7	-30
Brass	0	- 4.7	-10

15

The results with a positive gain in weight occur because of plating out of transients from the other specimens used in the test, and those metals that gained the transient weight virtually did not lose any weight due to corrosion themselves.

20

Example 2 - Corrosion Test/Laboratory

[ASTM #D-4340 (modified)]

This example examines corrosion of cast aluminum or magnesium alloys in engine coolants under heat rejecting conditions. Description: A cast aluminum alloy specimen, typical of that used for engine cylinder heads, or blocks, is exposed to an engine coolant solution temperature at 275°F (135°C) and at a pressure of 28 psi (193 kPa). An ASTM prescribed corrosive water is used to make up the water fraction of the 50/50 EG-water test coolant sample (Coolant "B"), which was not modified. The test is then modified for the subject coolant sample (Coolant "A"), so as to simulate true operating conditions of the non-aqueous PG coolant and system. Thus, not only is the use of corrosive water

35

- 25 -

eliminated, which renders operation of the test in a non-aqueous state, but the test pressure is also reduced to 2 psi (13.79 kPa), which is approximately ambient pressure.

5 A heat flux is established through the specimen and the test is carried out for one week, which is 168 hours. The heat transfer corrosion is measured by the weight change in the specimen, measured by the number of milligrams lost by the specimen. The test provides a  
10 critical evaluation of the coolant solution's ability to inhibit aluminum, as well as magnesium, corrosion at a heat rejecting surface.

#### Results

[ASTM #D-4340 (modified for Coolant "A"; 2 PSI)]

15

	$\Delta$ WT	$\Delta$ WT	
<u>METAL</u>	<u>"A" COOLANT (Mg)</u>	<u>"B" COOLANT (Mg)</u>	<u>ASTM STD.</u>
Aluminum	0.067	1.61	<2
Magnesium	0.18	5.79	<2

20

#### Example 3 - Field Test

A 3.8L V-6 engine was operated "over the road" for a test period of 55,000 miles (88,511.5 km). The vehicle was configured to the specifications of the 5,031,579  
25 patent and filled with subject coolant "A." There was no draining or replacing of the coolant during the test period. A metal specimen bundle was placed with the full flow of the engine coolant stream (lower hose) and was kept submerged in the coolant at all times.  
30 Performance of the test coolant's ability to inhibit metal corrosion was evaluated by comparing the results in milligrams lost of the specimen at the end of the test period to ASTM test standards.

- 26 -

In Service Vehicle Test Results

(Road Operation of 55,000 miles (88,511.5km))

	<u>METAL</u>	<u>Δ WT</u> <u>"A" COOLANT (Mg)</u>	<u>ASTM STD.</u>
5	Cast Iron	-2.8	-10
	Aluminum	+0.2	-30
	Steel	-1.1	-10
	Copper	-1.3	-10
10	Solder	-3.7	-30
	Brass	-0.9	-10
	* pH at start	+5.1	NA
	* pH at finish	+4.9	NA
	* (Testing requires the delution of 50% with water)		
15	While the preferred embodiment of the invention has been disclosed it should be appreciated that the invention is susceptible of modification without departing from the scope of the following claims.		

- 27 -

## CLAIMS

1. A method of cooling a heat exchange system which comprises circulating a composition in said system, said composition consisting essentially of propylene glycol, and at least one of a molybdate salt, a nitrate compound and an azole compound.

2. The method of claim 1 wherein said molybdate salt is sodium molybdate.

3. The method of claim 1 wherein said nitrate compound is sodium nitrate.

4. The method of claim 1 wherein said azole compound consists of tolyltriazole.

5. The method of claim 1 wherein said propylene glycol is present in a concentration of about 84.5% to about 99.85% by weight, said molybdate salt is sodium molybdate which is present in a concentration of about 0.05% to about 5.0% by weight, said nitrate compound is sodium nitrate which is present in a concentration of about 0.05% to about 5.0% by weight, and said azole compound is tolyltriazole which is present in a concentration of about 0.05% to about 5.0% by weight.

6. The method of claim 1 wherein said propylene glycol is present in a concentration of greater than 99.0% by weight, said molybdate salt is sodium molybdate which is present in a concentration of about 0.3% by weight, said nitrate compound is sodium nitrate which is present in a concentration of about 0.3% by weight, and said azole compound is tolyltriazole, which is present in a concentration of about 0.3% by weight.

SUBSTITUTE SHEET (RULE 26)

- 28 -

7. The method of claim 1 wherein the heat exchange system is an internal combustion engine heat exchange system.

5           8. The method of claim 1 wherein the heat exchange system is a motor vehicle engine heat exchange system.

10           9. The method of claim 1 wherein said propylene glycol is present in a concentration of about 84.5% to about 99.85% by weight, said molybdate salt is sodium molybdate which is present in a concentration of about 0 to about 5.0% by weight, said nitrate compound is sodium nitrate which is present in a concentration of about 0 to 5.0% by weight, and saidazole compound is tolyltriazole which is present in a concentration of about 0 to about 5.0% by weight.

20           10. The method of claim 1 wherein said propylene glycol is present in a concentration of about 99.0% to about 99.7% by weight, said molybdate salt is sodium molybdate which is present in a concentration of about 0 to about 0.3% by weight, said nitrate compound is sodium nitrate which is present in a concentration of about 0 to 0.3% by weight, and saidazole compound is tolyltriazole which is present in a concentration of about 0 to about 0.3% by weight.

30           11. A method of cooling a heat exchange system which comprises circulating a composition in said system, said composition consisting essentially of a mixture of propylene glycol and ethylene glycol, and at least one of a molybdate salt, a nitrate compound and anazole compound.

SUBSTITUTE SHEET (RULE 26)

- 29 -

12. The method of claim 11 wherein said molybdate salt is sodium molybdate.

5 13. The method of claim 11 wherein said nitrate compound is a sodium nitrate.

14. The method of claim 11 wherein said azole compound consists of tolyltriazole.

10 15. The method of claim 11 wherein said propylene glycol is present in a concentration of about 40.0% to about 98.85% by weight, said ethylene glycol is present in a concentration of about 1.0% to about 54.5%, said molybdate salt is sodium molybdate which is present in a  
15 concentration of about 0.05% to about 5.0% by weight, said nitrate compound is sodium nitrate which is present in a concentration of about 0.05% to about 5.0% by weight, and said azole compound is tolyltriazole which is present in a concentration of about 0.05% to about  
20 5.0% by weight.

16. The method of claim 11 wherein said propylene glycol is present in a concentration of about 40.0% to about 98.0% by weight, said ethylene glycol is present  
25 in a concentration of about 1.0% to about 59.0%, said molybdate salt is sodium molybdate which is present in a concentration of about 0.3% by weight, said nitrate compound is sodium nitrate which is present in a concentration of about 0.3% by weight, and said azole  
30 compound is tolyltriazole, which is present in a concentration of about 0.3% by weight.

17. The method of claim 11 wherein the heat exchange system is an internal combustion engine heat

SUBSTITUTE SHEET (RULE 26)

- 30 -

exchange system.

5 18. The method of claim 11 wherein the heat exchange system is a motor vehicle engine heat exchange system.

10 19. The method of claim 11 wherein said propylene glycol is present in a concentration of about 40.0% to about 98.85% by weight, said ethylene glycol is present in a concentration of about 1.0% to about 54.5% by weight, said molybdate salt is sodium molybdate which is present in a concentration of about 0 to about 5.0% by weight, said nitrate compound is sodium nitrate which is present in a concentration of about 0 to 5.0% by weight, and saidazole compound is tolyltriazole which is present in a concentration of about 0 to about 5.0% by weight.

20 20. The method of claim 11 wherein said propylene glycol is present in a concentration of about 40.0% to about 98.0% by weight, said ethylene glycol is present in a concentration of about 1.0% to about 59.0% by weight, said molybdate salt is sodium molybdate which is present in a concentration of about 0 to about 0.3% by weight, said nitrate compound is sodium nitrate which is present in a concentration of about 0 to 0.3% by weight, and saidazole compound is tolyltriazole which is present in a concentration of about 0 to about 0.3% by weight.

30

SUBSTITUTE SHEET (RULE 26)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/07659

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC(6) : CO9K 5/00 US CL : 252/74,75; 123/41.42 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) U.S. : 252/74,75; 123/41.42		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE search terms: propylene glycol, molybdate, nitrate, azole, tolyltriazole,		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US, A, 5,240,631 (MASCIOLI ET AL) 31 August 1993, Example I, Table 3 and col. 2, lines 12-18.	1-10 ----- 11-20
X	WO 89/09806 (RENY) 19 October 1989, Examples 1 and 2, page 7.	1-20
X,P --- Y,P	US, A, 5,422,026 (GREANEY) 06 June 1995, Example I, Table 3 and col. 2, lines 19-25.	1-10 ----- 11-20
X	US, A, 5,387,360 (UEKUSA ET AL) 07 February 1995, Table I, Example 8.	1-10
Y	US, A, 4,728,452 (HANSEN) 01 March 1988, Example 5, col. 3, lines 29-41.	1-20
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	"T"	Inter document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"G"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 16 JULY 1996	Date of mailing of the international search report 03 SEP 1996	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer <i>Mpendue Roy</i> fw CHRISTINE SKANE Telephone No. (703) 308-0661	

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**